not a substitute for curbing carbon dioxide emissions themselves. Middle-of-the-range scenarios of future increases in greenhouse gases forecast by the Intergovernmental Panel on Climate Change indicate that our atmosphere might, by the end of the twenty-first century, resemble that simulated for the Eocene.[77] Edward Jacob's fossils are a stark warning as to what the future climatic consequences of that drastic alteration to the chemistry of our atmosphere might be.

Chapter 8

Nature's green revolution

Scientific progress and new technologies frequently go hand in hand and, by the late 1960s, mutually beneficial advances in both led to the striking discovery of a novel photosynthetic pathway. The new pathway involved an upgrade in the form of a solar-powered, carbon dioxide pump that gave the owners the ecological upper hand in hot, dry climates and under conditions of carbon dioxide starvation. This revelation was soon followed by the dramatic discovery that grasses with the newly recognized photosynthetic pathway transformed the subtropics, converting forests to grass-dominated savannas in a geological instant late in the Miocene, some 8 million years ago. A sudden bout of carbon dioxide starvation was widely regarded as an obvious trigger for the rise of savannas, but this view fell out of favour when records showed that the atmospheric content had dwindled millions of years before their ecological success. In the search for new explanations, fire science is the smouldering favourite to offer a solution.

The farther researches we make into things, the more beauty and harmony we see in them.

Stephen Hales (1727), *Vegetable staticks*

THE scientific revolution of the seventeenth and eighteenth centuries, if indeed it can be recognized as such, saw the foundations of modern science established. Developments by iconic figures, notably Francis Bacon (1561–1626), Galilei Galileo (1564–1642), Robert Boyle (1627–91), and Isaac Newton (1642–1727), among others, advanced the study of the natural world by moving it away from mystical concepts and grounding it firmly in the rational. Bacon outraged his intellectual contemporaries with the belief that scientific knowledge should be built on empirical observation and experimentation, and pursuing this theme is alleged to have done for him in the end, at the age of 65. According to Bacon's former secretary, the legend goes that Bacon was travelling in a coach towards London with one of the King's physicians on a snowy day in April 1626 when he decided to investigate whether meat could be preserved by ice. Seizing the opportunity for an experiment, Bacon purchased a chicken in Highgate, then a small village outside London, gutted it, and proceeded to stuff the carcass with snow to see if it delayed putrefaction. In his excitement he became oblivious to the cold, caught a chill, and took refuge in the Earl of Arundel's nearby house in Highgate, the Earl being away serving time in the Tower of London. Bacon died a few days later, probably from pneumonia, after being put up in a guest room with a damp bed disused for over a year, but not before penning a letter to the Earl communicating the success of the experiment.

This delightful story of Bacon's ultimate demise would have been fitting for his contribution to modern science, but is probably apocryphal. Surviving records indicate Bacon was already ill before the end of 1625, and inclined to inhale opiates and the vapours of chemical saltpetre (potassium nitrate) to improve his spirits and strengthen his ageing body. In those days, the saltpetre was impure, a mixture of potassium nitrate, sodium nitrate, and other compounds

that may have given off toxic vapours. It seems possible, likely even, that Bacon overdosed on his inhalation of remedial substances to compensate for his ill health.[1]

As the scientific method became established, the world absorbed a deeper truth about humanity's place in the Universe, and the towering achievements of Bacon, Galileo, Boyle, Newton, and the other scientific greats set the agenda for the centuries ahead. The Cambridge historian Herbert Butterfield (1900–79) famously described the scientific revolution as being like 'putting on a new pair of spectacles', meaning it was central to defining our modern world.[2] But legitimate doubts remain about a version of history that claims the existence of a 'revolution'; suspicions linger that the concept is an artificial construct of historians.[3] We know, for example, that few people of the seventeenth century believed what scientific practitioners believed. In the days before communication highways like the Internet, the overwhelming majority of the population in England (and elsewhere) were completely unaware that the so-called scientific revolution was happening. Regardless of what we call it, knowledge of the natural world encompassing mathematics, physics, chemistry, and astronomy undoubtedly changed radically between the fifteenth and eighteenth centuries.

Lisa Jardine, a renowned historian at the University of London, persuasively argues for an alternative illuminating take on the development of 'classical' science.[4] Jardine wants us to recognize that the invention of instruments, and the pioneers who deployed them, critically underpin the scientific advances. Revolutions in technology went hand in hand with advancements in science. Technical instruments like microscopes, telescopes, pendulum clocks, balance-spring watches, and vacuum pumps catalysed the new science. These inventions gave the 'natural philosophers' a means of making original observations of the world around them from which theoretical foundations could emerge. This is how science progresses, and we should not find it surprising, when shifting our time horizon closer to the present, that significant recent discoveries also pivoted around new technologies and creative talents, much as the pursuit of science has always done.

Nowhere is this more apposite than in the sequence of momentous discoveries that eventually cracked the puzzle of how plants harness sunlight to synthesize biomass from carbon dioxide. The early roots of the puzzle date back to the Flemish natural philosopher, Jan Baptista Van Helmont (1577–1644) in the sixteenth century. Van Helmont conducted a pioneering experiment when he placed a willow cutting in dry soil and, after supplying it with no nutrients other than rain-water, recorded a 30-fold increase in mass.[5] He then rather spoilt it all by mistakenly arguing that the extra plant material—wood, bark, roots, and leaves—came from the water not air. This mistaken belief is quite common even today among producers of television gardening programmes in which the presenters exhort us to 'feed' our plants by adding food to the soil. Admittedly, the 'food' is required by plants to grow, but the basic building blocks for synthesizing biomass come from carbon dioxide extracted from the air.

Nevertheless, we should acknowledge Van Helmont's contribution for it called attention to the riddle of how plants grew. But it was not until the English clergyman Stephen Hales (1677–1761) reported in his remarkably perceptive 1727 book *Vegetable staticks* that 'plants [were] very probably drawing thro' their leaves some part of the nourishment from the air' that it started to become clear what was happening. Hales drew this correct conclusion after recording that plants had reduced the volume of air in a closed vessel by around 15%. Although Hales could not really account for the observation, thankfully his thinking was on the right lines because the air volume was reduced by the removal of carbon dioxide. Hale went on to muse how air was 'imbibed into the substance of the plant' and noted 'may not light also, by freely entering the surfaces of leaves and flowers, contribute much to ennobling principles of vegetation'. And well he might, for plants achieve the feat by the remarkable process of photosynthesis. I say remarkable for good reason: a photon of light travels 93 million miles (150 million kilometres) to reach the Earth's surface in about eight minutes, yet it takes a plant seconds to capture its energy, process it, and store it in a chemical bond. Endlessly fascinating, photosynthesis is exceptionally complex and of considerable antiquity, dating back at least 2.5 billion years. It has played a pivotal role in the affairs of our planet, as a recent congress of scientific experts on photosynthesis highlighted with their telling statement: 'photosynthesis: the plant miracle that daily gives us bread and wine, the oxygen we breathe, and simply sustains all life as we know it'.[6] For all this, and perhaps unsurprisingly, its great elegance and sophistication only became clear when new technologies were

brought to bear on the matter, some 300 years after Hales queried how it all worked.[7]

Foremost among the new technologies giving us the means to investigate the puzzle of photosynthesis was the cyclotron, a machine developed by the renowned nuclear physicist Ernest Lawrence (1901–58) at the University of California's Berkeley Radiation Laboratory. Really a progenitor of modern particle accelerators, the cyclotron provided scientists with a means of studying the transformation of elements by disintegrating atoms with charged particles accelerated through millions of volts.[8] Its invention ushered in the beginnings of the modern nuclear age, and while nuclear physicists got excited by the new machines, others quickly appreciated that they had much to offer when it came to investigating how plants grew.

Two talented young researchers, Samuel Ruben (1913–43) and Martin Kamen (1913–2002), arriving at the right place (University of California, Berkeley) at the right time (late 1930s), quickly seized the opportunity to exploit the new technology of the physicists to investigate the riddle of how plants harvest sunlight and use its energy to make organic acids and carbohydrates (see Plate 15).[9] Recognizing that by the late 1930s traditional ideas about photosynthesis were crumbling, Ruben and Kamen began pioneering experiments using radioactive carbon atoms produced by the cyclotron. Their idea was to replace the carbon atom in the carbon dioxide molecule with a radioactive form, thereby 'labelling' it before it was taken up by the plant. It is a deceptively simple technique. It means that radioactive (labelled) compounds can be easily distinguished from unlabelled non-radioactive compounds and provides a novel way of tracing the progress of carbon dioxide through the plant as it is metabolized. Ingenious though this line of research was, the radioactive form of carbon then available to them (^{11}C) quickly lost its radioactivity, falling by a half in 21 minutes.[10] The short half-life of ^{11}C frustrated their efforts, and despite hundreds of experiments the original goal of establishing exactly how carbon dioxide was processed inside leaves remained tantalizingly out of reach.

To make progress, and give Ruben and Kamen a genuine chance of finding out how plants metabolized carbon dioxide, the pair urgently needed a radioactive form of carbon with a longer half-life. For that, their attention once again turned to the Radiation Laboratory's cyclotron. Kamen performed what turned out to be a crucial experiment on a rainy 19 February 1940, which involved bombarding graphite with protons in the cyclotron. Shortly before dawn, he scraped the disintegrated graphite off the probe into a vial and placed it on Ruben's desk for analysis, closed down the cyclotron, and headed home to get some sleep. Wearily stumbling home, Kamen was apprehended by the police on the lookout for suspects in a series of gruesome murders. The dishevelled scientist fitted the bill. However, the sole hysterical survivor of the massacre failed to identify the suspect, and he was released to crawl home and collapse into sleep, only to be awoken some 12 hours later by an excited Ruben. The sample Kamen had produced was giving off a faint trace of long-lived radioactivity, suggesting that it was the long-sought-after form of carbon. After exhaustive checks, Kamen and Ruben finally announced their momentous discovery on 27 February 1940.[11] They had discovered a new radioactive isotope of carbon (^{14}C) that decayed by a half not in minutes, but over millennia.

The breathtaking discovery of this supremely important isotope by Kamen and Ruben proved a watershed in the use of tracers in every area of biological and medical research. But exploiting it to understand the mysteries of photosynthesis had to wait until the Second World War was over and, by that time, neither of these forgotten heroes of photosynthesis research was in a position to do so. Ruben died tragically on 28 September 1943 while working on a National Defence Research Committee project concerning chemical warfare. Sometime in September 1943 he had broken his right hand in a driving accident caused by falling asleep at the wheel. It was a seemingly minor event, but back in the laboratory the following Monday the injury made the usually straightforward task of plunging a small vial of phosgene gas into liquid air a difficult one. When the glass cracked unexpectedly, it released the deadly gas and Ruben inhaled a fatal dose. Kamen later summarized Ruben's outstanding but tragically short career:

> Ruben was responsible, almost single-handedly, for the growth of interest in tracer methodology... His unique combination of experimental skills, energy, wide-ranging interests, and quick grasp of essentials when confronted with new and unfamiliar areas of science, provided a focus for an ever-increasing number of able investigators.[12]

Kamen, meanwhile, had been removed from the Berkeley laboratory after (unjust) persecution by the House of Un-American

Activities Committee.[13] By July 1944, the Radiation Laboratory had been seconded into the war effort to produce radioisotopes for nuclear research in the Manhattan Project, an activity that intensified after the Japanese bombed Pearl Harbor on 7 December 1941. Following several years' secret research in this area at Berkeley, Kamen was declared a security risk, accused of being part of a 'spy ring' working for the Soviet Union. It left him deeply depressed and perplexed. A concerted campaign to clear his name in the courts followed and eventually saw his successful acquittal on all fronts. Kamen went on to enjoy a distinguished scientific career, receiving many honorary degrees and awards.[14]

By 1945, cyclotrons had become yesterday's technology, as the race to develop the atomic bomb spawned nuclear reactors. Nuclear reactors routinely produced large amounts of highly radioactive ^{14}C ideally suited for research on photosynthesis, making Kamen and Ruben's dream of discovering how photosynthesis works a reality. With Kamen and Ruben out of the picture, the opportunity to exploit the ready availability of ^{14}C fell to the team of scientists that Lawrence had newly installed at the Radiation Laboratory, Berkeley. The team was led by Melvin Calvin (1911–97), who oversaw an astoundingly productive 10-year period of research in collaboration with his colleagues Andrew Benson and James (Al) Bassham.[15] Driven by fierce competition with a rival group in Chicago, the team successfully elucidated the route by which plants produced their food from carbon dioxide and water.[16] Once again, the pattern of invention and discovery was repeated.

To get some flavour of the remarkable significance of the innovations and advances that have taken us to this point, it is worth noting that we have just breezed through the work of two Nobel Prizes, one awarded to Ernest Lawrence (Physics, 1939), the other to Melvin Calvin (Chemistry, 1961). The count rises to three if we include Ernest Rutherford (1871–1937) (Chemistry, 1908), whose concept of the atomic nucleus set the stage for Lawrence's ideas; four if we include the Prize awarded to John Cockcroft (1897–1967) and Ernest Walton (1903–95) (Physics, 1951), at the Cavendish Laboratory in Cambridge, for their pioneering linear particle accelerator that enabled them to split the atomic nucleus, one of the great scientific achievements of all time, and win the race against their American rivals.[17] Some time after Calvin received the 1961 Nobel Prize in Chemistry, he joined contemporary and former American Nobel Prize winners at the White House with President John F. Kennedy (1917–1963) and his wife. The event inspired Kennedy's famous quip: 'this is the most extraordinary collection of talent and human knowledge gathered at the White House, with the possible exception of when Thomas Jefferson dined here alone'.[18] Kamen and Ruben are the two most significant omissions from this list of Nobel laureates. Colleagues declared that 'there is no doubt that Ruben and Kamen unequivocally earned a Nobel Prize for their discovery of long-lived radioactive carbon (^{14}C), which engendered a revolution in humanity's understanding of biology and medicine'.[19] Others thought the Nobel Committee might have been more generous in awarding the Prize jointly to Calvin and his principal collaborator Andy Benson, to recognize the importance of Benson's intellectual and experimental leadership in the research that saw the pathway of photosynthesis revealed.[20]

Calvin and Benson's team showed that plants converted carbon dioxide into a compound with a backbone of three carbon atoms, which subsequently feeds into a biochemical cycle to produce organic acids.[21] The cyclical conversion of carbon dioxide to organic acids and then sugars is catalysed by the enzyme Rubisco (see also Chapter 3, p. 49), of which we shall learn more later.[22] The details describe a universal process that explains how plants grow, and clarifies our understanding of the intermediate steps in the pathway; explaining and clarifying, two of the most satisfying attributes of a scientific discovery.[23] Afterwards, pretty much all plants were believed to process carbon dioxide in this way and became labelled 'C_3 plants', the C_3 terminology referring to the number of carbon atoms in the first molecule created when plants take up carbon dioxide. Thirty years on, though, it was becoming obvious that this simple view of the plant world was wide of the mark. The puzzle began when scientists at the Hawaiian Sugar Planters' Research Laboratory, Honolulu, noticed something odd when studying sugarcane: the radioactively labelled carbon turned up in organic acids with a four-carbon backbone instead of the expected three.[24] Other Russian and Australian scientists studying maize and salt marsh plants noticed the same oddity.[25] Indeed, the business of the four-carbon organic acid was so odd that the Russian scientist queried his experimental procedures.

None of this biochemical confusion escaped the attentions of our next two scientists, who went on to make an astonishing

contribution. Ruminating over a few glasses of beer, that well-worn path to scientific progress, the Australian Hal Hatch and Briton Roger Slack resolved to take up the challenge and understand what, if anything, the four-carbon oddity meant. Pretty soon the duo uncovered something special. In a dazzlingly productive 5–6-year phase from 1965 onwards, they discovered that tropical grasses had evolved a revolutionary upgrade to the mode of photosynthesis recognized by Calvin, Benson, and their team.[26] The elaborate upgrade comes in the form of a solar-powered carbon dioxide pump boosting the carbon dioxide concentration around the enzyme—Rubisco—catalysing the synthesis of sugars.[27] In this mode, carbon dioxide is first captured and attached to a special carrier compound, which is then pumped into a special 'wreath-like' arrangement of cells surrounding the leaf veins. Inside these cells, the carrier's cargo is detached to create miniature carbon dioxide-rich greenhouses.[28] The arrangement boosts the concentration of carbon dioxide inside the cells to ten times that in the atmosphere and, bathed in this luxurious carbon dioxide-rich environment, Rubisco converts carbon dioxide into organic acids and then sugars with supreme efficiency, one unmatched by any other group of plants.[29] It is no surprise to learn, then, that C_4 plants rank amongst our most productive crops and worst weeds. The four-carbon compound puzzling the workers in Hawaii, Russia, and Australia turned out to be the carrier compound shuttling carbon dioxide into the special wreath-like cells. The discovery of the so-called C_4 photosynthetic pathway sealed the fame and honour of Hatch and Slack, who had given science a glimpse of the hidden internal workings of C_4 plants. When Hatch modestly revealed the circumstances surrounding the discovery of C_4 photosynthesis years later, we find they too echo Kamen and Ruben's discovery of ^{14}C:

> I think I am supposed, on occasions like this, to say how it is done. This reminds me of the situation when centenarians are asked what their secret is. Half say clean living and no drinking or smoking, the other half say the complete opposite. It may sound trite but it is true that luck is a most critical factor—just getting to be in the right place at the right time.[30]

As is so often the case with a new discovery, previously confusing observations fell into place. As early as 1884, the great German botanist Gottlieb Haberlandt (1854–1945) had bequeathed the term 'Kranz' to describe the special arrangement of cells inside the leaves of certain plant species, without appreciating their functional significance.[31] With the discovery of C_4 photosynthesis the arrangement made sense. The cells separate the two biochemical systems involved in processing carbon dioxide and its products spatially, a convenient division of labour within the leaf. Especially permeable to metabolites, this special arrangement of cells is remarkably impermeable to carbon dioxide. Kranz anatomy, or in modern parlance, the bundle sheath, is now recognized as a characteristic feature of the leaves of most species of C_4 plants.[32]

The C_4 photosynthetic pathway compensates for a deeply embedded evolutionary compromise in Rubisco, the enzyme at the heart of photosynthesis. The enzyme originally evolved in photosynthesizing micro-organisms called cyanobacteria nearly 3 billion years ago, when the atmosphere contained around 100 times more carbon dioxide than now and negligible amounts of oxygen.[33] Such a plentiful supply of carbon dioxide boosted photosynthesis for the entire biosphere, a planet-wide version of the C_4 pump allowing Rubisco to operate with maximum efficiency. When land plants inherited a version of Rubisco from cyanobacteria, who themselves ultimately became transformed in the critical photosynthetic organelles called chloroplasts,[34] the atmosphere contained only a tenth as much carbon dioxide. This shift in the atmospheric composition exposed a serious problem for Rubisco, the enzyme with an undeserved reputation for being slow and wasteful.[35] Starved of carbon dioxide, Rubisco splutters along, like an engine starved of fuel, often backfiring by capturing molecules of oxygen instead of carbon dioxide. When this happens, C_3 plants waste solar energy and lose valuable carbon dioxide. C_4 plants, equipped with their photosynthetic upgrade, avoid the pitfall but pay the price, if it can be considered as such, of generally being restricted to a subtropical existence where the warm climate is best suited to drive the pump. All of which points to the C_4 way of life as an adaptation to carbon dioxide starvation,[36] with a drop in the greenhouse gas millions of years ago having a decisive hand in the evolution of this novel photosynthetic pathway.[37]

Spanning three decades, the entwined chain of technological progress and discovery linking the beginnings of the nuclear age to the

mysteries of Hawaiian sugar plantations saw nature's revolution—plants with the C_4 photosynthetic pathway—finally drawn to the attention of the scientific community. The current situation is that we recognize approximately 7500 species of C_4 plants, occupying a fifth of the vegetated land surface of our planet and accounting for 30% of the primary productivity of the terrestrial biosphere.[38] By far the majority are subtropical grasses, although some sedges and herbs have also benefited from the revolution.[39] Because their biochemical machinery operates most efficiently at high temperatures and in bright sunlight, it confines most C_4 plants to subtropical climates, where they dominate the grasslands and savannas. Only a single species of tree is known to use C_4 photosynthesis, *Chamaesyce forbesii*, and it occurs on Hawaii, an island where evolutionary pressures are altered by millions of years of isolation. Other than *C. forbesii*, the closest we have to a C_4 tree are a few woody shrubs that approach tree-like status with advanced age, notably black saxaul (*Haloxylon aphyllum*) in the hot, sandy deserts of central Asia.

It is a peculiar irony that C_4 plants only belatedly came to be recognized by modern science. For not only have we been exploiting them as part of our own agricultural revolution for the past 10 000 years, oblivious to their secret, but they also set the scene for the evolution of our ancestors.[40] Maize and sugarcane, the two blockbuster C_4 crops, had far-reaching impacts on society. Maize, domesticated from its wild ancestor teosinte somewhere in the western highlands of Mexico about 7500 years ago, spread across Mesoamerica, paving the way for the rise of complex pre-Columbian civilized societies in the Americas. Sugarcane was domesticated in New Guinea and has been known to history since the time of Alexander the Great (356–323 BC). It spread throughout the Caribbean in the seventeenth century, providing a cheap supply of sugar to the Western world and creating a revolution in human societies by altering our diets, social customs, and economies. Cultivating sugarcane is a labour-intensive business and large numbers of Africans were kidnapped and sold into slavery in the Caribbean to tend plantations, events that irreversibly changed the social fabric of the region. We may have tamed C_4 crops, but they have also tamed us by exerting a powerful influence on human social evolution and persuading us to cultivate them.

So, did chance alone create the elaborate and successful C_4 revolution in the plant world or is there more to it than that? Any account might sensibly begin with the question of when C_4 plants evolved. It is an obvious one to ask, but a difficult one to answer. The fossil record of grasses is pitiful. Rarely are the organic remains of grasses preserved as fossils because grasslands, by their very nature, occur in arid regions. The distinction of being the undisputed oldest known leaf fragments of a fossil C_4 grass goes to those recovered in 1978 from the appropriately named Last Chance Canyon in southern California.[41] Misdating of the sediments meant it was not recognized as the record holder until later, when the accepted age was established to be 12.5 million years old (Miocene age). Some scientists have tried to stake a claim for discovering the oldest ever C_4 grass, pushing back the date by 1.5 million years,[42] but their claim is based on tenuous evidence, the fragmentary remains of grass cuticles, and has been roundly rejected. Other than a fossil grass splinter with Kranz anatomy recovered from 5–7-million-year-old Miocene sediments in north-western Kansas,[43] this is the unsatisfactory sum of evidence the fossil record of leaf remains has revealed so far.

Fortunately, we can peer further down the historical corridor of C_4 plants to estimate the timing of their origins with molecular clocks. Molecular clocks are founded on the observation that the genetic code of all organisms—DNA—undergoes steady mutations over time in a fashion analogous to the ticking of a clock. These mutations are, in Charles Darwin's prescient phrase, 'neither beneficial or injurious'.[44] If the mutation rate is known, then if we know the number of mutations that separate the DNA sequences of species that once shared a common ancestor, it is possible to estimate the time that has elapsed since they diverged. For C_4 plants, grasses are the last common ancestor and their earliest unequivocal origins date to 50–65 million years ago.[45] These dates suggest that the (non-avian) dinosaurs did not eat grasses, but this idea was turned on its head only recently with the surprise discovery by a team of researchers from the Swedish Natural History Museum of microscopic silica structures characteristic of grasses in dinosaur droppings.[46] One group of grasses, the Poaceae, evidently originated and had already diversified in the Cretaceous, suggesting that the picture is not as clear-cut as originally thought. Still, molecular clocks of grasses calibrated against another ancient family of grasses, the Panicoideae, place the origins of C_4 plants at 25–32 million years ago, considerably younger than the palaeontological dates.[47]

At first sight, the enormous discrepancy between molecular and palaeontological dates for the origination of C_4 plants appears irreconcilable. Rapprochement, however, is closer than it seems. We should not expect the fossil record to provide the earliest date of C_4 plant origins. In all likelihood, C_4 photosynthesis evolved well before the 12.5-million-year-old Last Chance Canyon fossils; it is just that the plants using it were scarce in the ancient floras and the conditions for preservation as fossils were unlikely to be common in arid environments, making the fossils rare. Molecular clocks, too, are not without error. Uncertainties in the rates of mutations bedevil their time-keeping properties. All things considered, though, the molecular dates are probably the best indication we have for when C_4 plants originated. If we accept a date of 30 million years ago, it means the revolution sparked into life comparatively recently; compressing the entire time plants have occupied our planet into a single 24-hour day, C_4 plants arrive at the party around ten-thirty in the evening.

The story moved on when, throughout the 1980s and 1990s, a team of researchers at the University of Utah reported remarkable results from analyses of fossil teeth.[48] The researchers focused on the teeth of herbivorous mammals because their isotopic composition reflects that of the plants they consume. As Hatch and Slack showed, C_4 plants fix carbon dioxide differently compared to C_3 plants, and it later transpired that this results in them containing a different abundance of the heavy and light stable isotopes of carbon, a difference that is passed on to carbon-containing tissues, like the teeth and bones of the animals that eat them.[49] On the Athi Plains in Kenya, for example, where C_3 and C_4 plants coexist, grazing zebras preferentially select C_4 grasses and have teeth with an isotopic composition distinct from that of giraffes browsing C_3 trees and shrubs.[50] From the isotopic perspective, at least, we can see that fossil teeth speak to us about the dietary habits of their long-since-departed owners, who wandered the plains of ancient continents millions of years ago.

What the scientists from Utah learned, straight from the horse's mouth, as it were, was that the rise of C_4 grasses had been nothing less than meteoric (Fig. 13). Before 8 million years ago, C_3 trees and shrubs dominated the diets of large herbivorous mammals like zebras and horses in Africa and the Indian subcontinent. Within about a million years, however, the fossil teeth revealed a dramatic near-synchronous

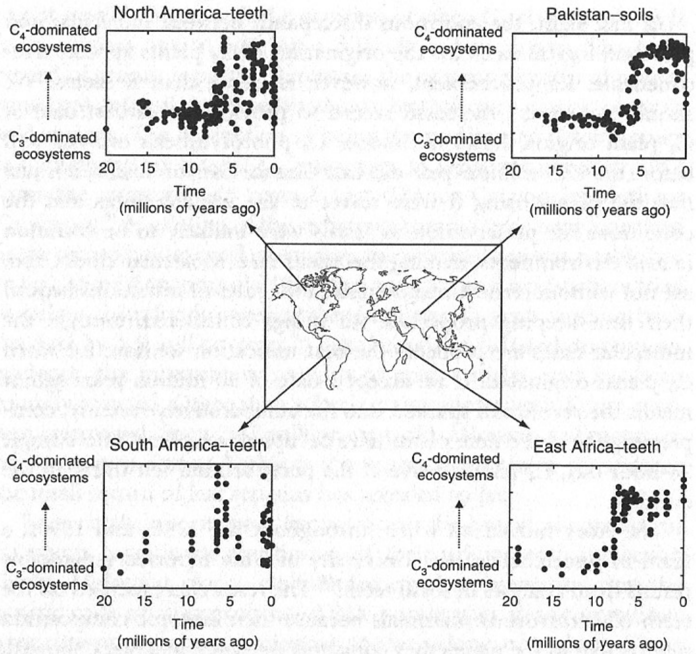

Fig. 13 The global rise of C_4 plant dominance in terrestrial ecosystems inferred from the isotopic composition of fossil tooth enamel and soils.

worldwide switch to diets consisting entirely of C_4 grasslands.[51] The switch implied that C_4 grasses exploded onto the ecological stage about 8 million years ago to replace former forests with C_4 savannas and grasslands. In the northern hemisphere, C_4 savannas originated in a latitudinal wave sweeping around the Earth from the hot tropics of eastern Africa to the cooler climes of North America. The rise of C_4 plants remains one of the most profound transformations of global ecosystems yet discovered in the fossil record, and its discovery ranks as one of the great triumphs in the field of modern isotope geochemistry. It also suggests the cradle of C_4 photosynthesis lies deeply hidden in the tropics. The S-shaped curves marked out by the painstakingly acquired isotope records from four continents (Fig. 13)

suggest we have ratcheted irreversibly towards the modern condition—a C_4 world.

Such profound changes in world vegetation demand explanation, and in the search for some answers attention focused on the fact that C_4 grasses had risen to dominate in the subtropics nearly synchronously in diverse geographic regions. This is strongly suggestive of a global trigger for the phenomenon and an obvious candidate is the carbon dioxide content of the atmosphere. So it was no surprise that researchers came up with a bold explanation, in the form of what we can call the 'carbon dioxide starvation' hypothesis.[52] According to this, dwindling carbon dioxide levels spelled double trouble for C_3 plants, starving them of carbon dioxide and water. This is because to combat carbon dioxide starvation they keep the microscopic stomatal pores on their leaves open wider for longer, causing more water to be lost by evaporation. Falling carbon dioxide in other words is equivalent to falling rainfall. C_4 plants, on the other hand, enjoyed immunity to both effects. Their superior photosynthetic pathway allows them to be productive under conditions of carbon dioxide 'starvation', and keep their stomatal pores closed when necessary to conserve precious water supplies. The Utah team argued that as the carbon dioxide content of the atmosphere breached some threshold value, it handed the ecological initiative to C_4 plants in hot climates. They concluded that

> the persistence of significant C_4 biomass beginning about 6–8 Myr [million years] ago and continuing to the present is compatible with atmospheric CO_2 levels in the Miocene declining below some 'crossover' point where C_4 grasses are favoured over C_3 grasses or other plants.[53]

It is a beguiling hypothesis, and understandably soon gained widespread acceptance as the leading explanation for the dramatic expansion of C_4 grasslands. It quickly found support from investigations revealing how tropical vegetation responded to the much more recent episode of carbon dioxide starvation that took place during the last ice age, a mere 20 000 years ago. The evidence, fossilized molecules of C_3 and C_4 plants, is preserved in lake sediments on tropical mountains in eastern Africa and in soils from the Chihuahuan Desert, New Mexico. Tracing the history of C_4 grasses in tropical Africa back to the last ice age reveals that they dominated mountain tops when the atmospheric carbon dioxide concentration was 50% lower than today, but as carbon dioxide levels rose they became replaced by C_3 forests.[54] It was a similar story in the Chihuahuan Desert: ice age, C_4 grasslands were abruptly replaced by C_3 desert shrubs about 9000 years ago, the time when carbon dioxide levels rose.[55] So, the 'carbon dioxide starvation' hypothesis scored two successes, elegantly explaining changes in tropical vegetation since the last ice age. Moreover, if these changes are achieved in a few thousand years, what is the capacity of carbon dioxide to restructure Earth's vegetation over millions of years?

Attractive though the 'carbon dioxide starvation' hypothesis is, it soon encountered a major obstacle. Serious difficulties surfaced with the publication of a carbon dioxide record in the international journal *Science* based on chemical analysis of the remains of marine phytoplankton in sediment cores drilled from the floor of the south-west Pacific Ocean.[56] According to the record, carbon dioxide levels had remained low geologically speaking (that is, similar to modern levels) between 5 and 16 million years ago. Later, two other approaches gauging the carbon dioxide content of the ancient atmosphere supported the same general picture.[57] All the evidence pointed to the onset of low carbon dioxide conditions 11 million years before the C_4 grasslands expanded, and a mismatch of this duration is not easily explained away.

If the atmospheric carbon dioxide records generated in the past decade render obsolete the idea that carbon dioxide starvation triggered the ecological success of C_4 grassland, it reinstates the search for other possible explanations. Our main clue to identifying what might have happened lies with the realization that the teeth and other isotopic records from the Old World are actually revealing a shift from subtropical C_3 forest or woodland to open savanna-style C_4 grasslands.[58] If forests are present, then they effectively exclude C_4 grasses, which cannot tolerate the cooler, shadier conditions. Deforestation, though, by whatever means, creates an open habitat, which if the climate is hot enough, allows the invasion of photosynthetically superior C_4 grasses. So what we are really searching for is a natural means of deforestation, a process that can only be brought about by climate change, and disturbance by fire and grazing animals.

Climate change over the long term (i.e. millions of years) is often driven by slow tectonic processes like the uplift of mountain ranges, and changing continental configurations that alter atmospheric and ocean circulation patterns governing the Earth's environment.

We can glimpse the consequences of climate change for forests and grasslands with a pilgrimage to the Siwalik formation, a thick band of sediment and rock much beloved by geologists that stretches through Pakistan, northern India, and Nepal. South of the Siwalik sediments in Pakistan, in the province of Baluchistan, lie the famed Bugti Bone Beds. The Bugti Bone Beds are older than the Siwaliks, and have inspired the imaginations of palaeontologists for over 200 years since yielding up the bones of the largest land mammal of all times, a giant rhinoceros called *Paracerathium*; shaped like a giraffe, it stood 5 m tall at the shoulder.[59] Compacted into the younger Siwaliks further north is evidence for changes in the vegetation, fauna, and climate of the region over the past 18 million years. The richly detailed sediments are a remarkable repository of Earth history and give us an insight into climate changes during the C_4 revolution in that part of the world. We find that as the revolution gathered pace and the C_4 savannas expanded, the Indian monsoon intensified causing the climate to dry and the once plentiful wintertime rains fail to appear.[60] Why the monsoon changed abruptly is still the subject of vigorous debate. On the one hand, uplift of the Tibetan Plateau around 8 million years ago has been found to do the job admirably in climate models.[61] On the other hand, some geologists believe the Plateau was already in place long before this.[62] Whatever the cause, with rains only appearing in the summer tree populations declined as recruitment of seedlings unable to survive the warm, dry winters failed. Forest deterioration inevitably followed, giving C_4 grasses the opportunity to take hold in the foothills of the Himalayas and the floodplains of the Ganges.

History tells us, then, that climate change can cause the decline and fall of C_3 forests and the establishment of C_4 grasses, but this is unlikely to be the whole story. There are other important influences at work that we are only beginning to appreciate. Exciting new detail was added to the picture when the South African workers William Bond and Guy Midgley realized they could improve upon the 'carbon dioxide starvation' hypothesis.[63] Thinking radically, they realized there was another way of looking at the problem, one integrating roles for climate change and wildfire. Instead of relying on a drop in carbon dioxide, their idea recognized that gaps in the forest, created by the death of trees during drought, allowed the establishment of patches of C_4 grasses. It is a seemingly small victory for the grasses.

Yet once the establishment of these apparently innocuous patches of grasses got underway, it supplied highly combustible fuel loads in the dry season that increased the flammability of the ecosystem. More frequent fires are more likely to kill more trees, which, in turn, allow the further ingress of C_4 grasses better adapted to recover rapidly after a burn by sprouting from underground rhizomes. In Bond and Midgley's scheme of things, a self-reinforcing fire cycle accelerates deforestation and promotes grassland expansion.

The question raised by this speculation is whether invasion by C_4 grasses really produces the dramatic alterations to the fire regime of the landscape they invoke. Certainly, it is hard to overestimate the role of fire in shaping the world's vegetation patterns. In today's world, fire maintains more than half the land surface currently classified as savanna.[64] Without regular wildfires, modern forests could double in size, shrinking the extent of our tropical grasslands and savannas, like those in South America and South Africa, by a half. Evidence for C_4 grasses promoting fire activity and retarding forest development is found in Hawaii and the South Pacific island of New Caledonia. In Hawaii, the ecological drama plays out in the woodlands of the Volcanoes National Park, where invasion of two introduced species of C_4 perennial grasses (*Schizachyrium condensatum* and *Melinus minutiflora*) began in the late 1960s.[65] Before grasslands invaded, minor fires broke out once every other year. Twenty years later and the fires are three times more frequent and 50 times as large. Grass invasion apparently set in motion a positive feedback cycle efficiently converting non-flammable native woodland into highly flammable C_4 grasslands, eliminating endangered plant species in the process. Similar trends are being observed in New Caledonia, where deliberate fires on the drier side of the island have allowed alien C_4 grasses to invade the tropical rainforests.[66] The situations in Hawaii and New Caledonia represent an analogue, telescoped in time and space, for the more ancient spread of C_4 grasslands across the surface of the Earth. And these modern wars of grassland attrition are taking place against a background of rising atmospheric carbon dioxide concentrations, arguing for fire as the more important agent accelerating the conversion of C_3 forest to C_4 grassland.

Taking our cue from observations of this nature, it seems plausible that fire contributed to the ecological success of the C_4 grasslands

millions of years ago.[67] However, observations by atmospheric physicists are revealing that even this hypothesis falls short of the complete picture because we are, in all likelihood, underestimating how powerfully fire could affect the spread of grasslands. Remarkable meteorological observations taken above the dense smoke produced by the hundreds of deforestation and agricultural wildfires that burn each year during the dry season in Amazonia are now revealing new connections between smoke, clouds, and climate. The fires burn at the boundary between tropical forests and C_4 grasslands and offer a unique insight into the consequences of fire-driven regime change millions of years ago. As we shall see, many of these findings shed new light on understanding how fire might reinforce the spread of C_4 grasslands by altering climate.

One of the first of the new connections between smoke and clouds was revealed by a young researcher, Ilan Koren, soon after he arrived at NASA's Goddard Space Flight Center in Maryland. Armed with a freshly minted doctorate from the University of Tel Aviv, Koren eagerly set about investigating the effects of tiny airborne particles produced by smoke on clouds using some of the world's most advanced satellite technology. He scrutinized satellite images taken above fires burning in the Amazon jungle during the dry season and quickly noticed that few, if any, showed clouds and smoke together—was smoke somehow suppressing cloud formation? Delving deeper into the phenomenon revealed why. Thick smoke plumes from fires travel for hundred of kilometres, shutting out sunlight and preventing it from reaching the ground. This effect slows evaporation on the ground and dries the air. Meanwhile the darker, smoky atmosphere above absorbs sunlight and warms up. Together, both effects reduce the flow and moisture content of the air needed to form certain types of clouds.[68] As Koren remarked, clouds really do seem to be 'nature's way of drawing in the sky the physics of what exactly is going on in the air'.

Clouds above the forest fires in Amazonia held further surprises for another team of researchers led by Meinrat Andreae at the Max Planck Institute for Chemistry in Mainz, Germany.[69] Andreae's team reported that smoke from the fires added huge numbers of aerosol particles to the atmosphere. An innocuous enough observation until it is realized that cloud droplets form when water vapour condenses around aerosol particles in the air. Thousands of droplets have to collide to form a drop large enough and heavy enough to fall as rain. Above the Amazon, the researchers found that smoke from fires increased the number of particles and dramatically reduced the size of the water droplets to the point where they were often not heavy enough to coalesce and fall as raindrops. Smoke from burning forests actually seemed to reduce rainfall.

From the trail-blazing work above the Amazon Basin came a new idea—wildfire can influence climate, and not just in the tropics. We usually think of a long hot spell of weather without rain as creating tinder-dry conditions that make natural and managed ecosystems prone to fire, placing agencies charged with fire management on a state of high alert. The reverse argument is that wildfire itself can influence climate to exacerbate the situation. In late April 1988, just such an effect was seen in the northern United States when the region experienced a severe drought, one of the driest of the twentieth century. Hundreds of thousands of acres of forest in the Yellowstone National Park burned in July of that year, adding vast amounts of black smoke to the atmosphere. One of the reasons for the severity of drought is believed to be the intense wildfires themselves. Smoke from the fires may have reduced cloud formation and disrupted atmospheric circulation patterns in the Midwest to an extent that this usually reliable and important source of precipitation for the region failed, exacerbating drought and priming the area for more fire.[70]

The expansion of C_4 grasslands millions of years ago, then, might be viewed as the Earth's switch to a flammable planet—a change accelerated by feedbacks causing climate change and more fire. The novel interactions between fire, trees, grasslands, clouds, smoke, climate, and carbon dioxide were more pervasive than at any time in Earth's history and form part of an intricate web of feedbacks (see Plate 16).[71] The complexity of the web can be analysed by representing each feature of interest as a node and connecting nodes in a linked chain of cause and effect by a series of arrows. The effect of one thing on another is examined and judged to be either positive or negative. A positive effect means more of one thing leads to more of another; a negative effect, indicated by a red mark, means more of one thing leads to less of the other. When a closed loop is identified by tracing out a pathway in a single direction from its start point to the end, the number of positives and negatives are summed to

determine the final sign of the loop. This approach to breaking down a complex network into its component parts, systems analysis, is borrowed from information theory, widely used in social science, economics, chemical engineering, and circuit design.

The remarkable point to notice about the complex web that sums up the current state of affairs for C_4 plants is that by far the majority of the newly identified feedback loops are strongly self-reinforcing, creating a situation that has promoted and sustained C_4 grasslands for millions of years (positive). The implication is that once the system is pushed beyond some threshold point, perhaps by a change in climate, forest deterioration accelerates inexorably towards a new stable state of flammable C_4 grasslands. In this more complete view of how the world works, we can see that the apparent ratcheting towards a C_4 world implied by the records from fossil teeth appears to be inevitable.[72]

We should note that the proposed network does not rely on a drop in the carbon dioxide content of the atmosphere, but does require the observed conditions of carbon dioxide starvation to prime the system. Carbon starvation limits the growth of tree seedlings, preventing them from reaching the minimum height required to become fireproof. Put another way, when carbon dioxide is scarce, forest recruitment becomes extremely vulnerable to fire. Accepting this scenario for now means we can reprise the role for carbon dioxide starvation by viewing it as a necessary pre-condition for giving C_4 grasslands the ecological upper hand as they increase the flammability of ecosystems and wipe out the forests. Interestingly, C_4 plants may even fortuitously maintain this situation by enhancing the slow removal of carbon dioxide from the atmosphere by the chemical weathering of magnesium and calcium silicate rocks, at a time when the contribution by deteriorating forests is otherwise relaxed. More weathering helps ensure that an atmosphere impoverished in carbon dioxide continues, reinforcing the C_4 existence at the expense of C_3 trees.

It has to be said that as yet there is little evidence to support the idea of a set of self-reinforcing feedback loops amplifying the ecological success of C_4 grasslands in the Old World. Still, whatever the plausibility of the interpretation, the ecology and atmospheric physics underpinning it are sound. And one possible expression of the positive feedbacks is found on the floor of the western Pacific Ocean.

It is, perhaps, hard to imagine a more unexpected destination for the combustion products of wildfire. Yet soot and charcoal are extremely resistant to chemical and microbial attack, and that transported on the trade winds from the Indian subcontinent to the Pacific has rained down through the depths to steadily accumulate on the seafloor for millions of years. Analysis of these deep ocean sediments reveals a striking thousand-fold increase in charcoal particles around 8 million years ago.[73] The charcoal contains charred fragments of grasses and wood, blackened remains testifying to the aggressive removal and replacement of one group of plants by the other. Although the record is patchy, it suggests that an increase in charcoal flux lags behind the conversion of forests to grasslands in India and Pakistan by about a million years. If the feedbacks operated in the sequence of climate change, vegetation response, and then fire, this lag is exactly what we would expect. It is too early to say if this is the smoking gun for regime change in the subtropics; the data are too sparse in the critical region of transition to make this out. The outlook is bright, however, because it is certainly not beyond the reach of modern geochemistry to bring the picture into sharper focus.

When astrophysicists started to unravel the mysteries of the Universe, they were struck by the long list of coincidences that suggested life depends very sensitively on the form of the physical laws and the values nature assigns to particle masses, force strengths, and the like.[74] The astrophysicist Fred Hoyle (1915–2001) was so impressed by what he called the 'monstrous series of accidents' that he commented that the Universe looked like a 'put-up job', meaning the laws of physics seemed finely tuned for life to appear.[75] As we unravel the hidden mysteries of C_4 plant success to reveal a web of feedbacks all leading in the same direction, we cannot help but wonder, in a less cosmic way, whether a C_4 world is also in Hoyle's words a 'put-up job'. If the carbon dioxide content of the atmosphere wasn't impoverished, if the climate hadn't changed, if grasses did not promote and tolerate fire, if C_4 grasses did not flourish under conditions of carbon dioxide starvation, if smoke did not beget drought and lightning. If only. The list of coincidences is impressive.

Impressive as it is, the question remains: why did C_4 plants leave it so late in the evolutionary day to appear on the ecological stage? Flowering plants evolved about 150 million years ago; C_4 plants failed to appear for another 120 million years. The obvious answer is that evolving the C_4 photosynthetic pathway is a difficult business. Complex changes in the expression of genes governing and regulating photosynthesis must be coordinated with those for other intricate metabolic processes and alterations to leaf anatomy.[76] Yet in spite of all this, we know that the C_4 photosynthetic pathway evolved independently from C_3 ancestors on at least 40 separate occasions.[77]

One of the reasons for multiple origins of C_4 plants may be that many C_3 plants possess components of the biochemical machinery necessary to conduct C_4 photosynthesis.[78] Celery (*Apium graveolens*) is an archetypal C_3 plant that has dimly lit green photosynthetic cells embedded inside the thick ridges of its stalks. In cut stems, these strange cells show up as green circles neatly aligned around the periphery. The explanation for the corridor of green through celery stalks is that it provides a means of recapturing carbon dioxide produced by respiring tissues (stems and roots) that might otherwise be lost as it leaked back to the atmosphere. In a surprise discovery, British researchers found that the clusters of green cells used the same enzyme as C_4 plants to strip the carbon dioxide from the four-carbon carrier compound found in the sap of C_4 leaves. The cells then convert it into organic acids with Rubisco through the pathway Calvin, Benson, and colleagues elucidated in the 1950s.[79] The working hypothesis here is that celery stalks perhaps function like an enlarged version of a C_4 leaf.

This exciting finding raises many questions. We don't yet know when C_3 plants evolved the capacity to manufacture C_4 plant enzymes and deployed them to scavenge 'waste' carbon dioxide. Could it be that recapturing carbon dioxide dissolved in sap represents some initial step on the road to C_4 plant evolution? Plant groups far more ancient than celery, like ferns and conifers, also have the capacity to do it, raising the possibility that C_4-type photosynthesis is much older than we think.[80] Could it be that plants 'learned' the trick millions of years ago and lost it, only to 'rediscover' it again more recently in their geological history? Our best guess about when it might have first been acquired is in the Carboniferous, 300 million years ago, when an atmosphere impoverished in carbon dioxide but enriched in oxygen prevailed for some 30 million years (see Chapter 3).[81] But so far no compelling evidence of C_4 photosynthesis in fossil plant remains dating to the Carboniferous and Permian has been unearthed.[82] If C_4 plants are 10 times older than we think and full-blown C_4 photosynthesis did arise so far back in time, it is well hidden indeed.

Getting to the bottom of questions like these is likely to be increasingly important in the coming decades. Thomas Malthus (1766–1834), the persistent pessimist who went on to become Britain's first professor of political economy, pointed out in his groundbreaking *Essay on the principle of population* of 1798 that the human population has the power to grow geometrically by repeatedly doubling over time. He concluded that the growth of food production would not keep up with that of the human population, writing 'the human species would increase in the ratio of 1, 2, 4, 8, 16 . . . etc. and subsistence as 1, 2, 3, 4, 5 etc.' The spectre of population catastrophe loomed large but, of course, Malthus's forecast turned out to be wrong. Contraception eased birth rates, to slow the explosive rise of the human population from the 1970s onwards, and the green revolution in the late 1960s, engendered by shrewd genetics and the production of nitrogenous fertilizers, ensured that world cereal production trebled in the second half of the twentieth century.

Feeding the world in the second half of the twenty-first century could be a different matter. The global human population is predicted to reach 9 billion by 2050.[83] Meeting the escalating world food demand may call for a second green revolution, one that has its roots in nature's own C_4 uprising. The scope for engineering a better version of Rubisco in C_3 crops like wheat, barley, soybean, and potatoes to raise yields and meet the burgeoning demand is limited. An alternative solution may be to transfer the superior C_4 photosynthesis into our C_3 crops to achieve this end. With this ambitious goal in mind, the attention of the plant biotechnologists has focused on rice, the world's most important staple C_3 crop. Global production of rice has risen threefold over the past three decades, but yields are expected to peak shortly as the crop reaches its maximum efficiency in converting sunlight into food. Because the land area available for cultivation is limited, feeding the world with rice will mean boosting yields by growing a bigger crop with harder-working Rubisco.[84] One way to do this will be to re-engineer rice with the turbo-charged

photosynthetic apparatus of C_4 plants.[85] Encouraged by the multiple origins of the C_4 pathway, the molecular geneticists believe it simply cannot be that difficult to do; the molecular engineering of C_4 rice is arguably the 'next frontier' in crop science, and a goal several decades away. But will success in this endeavour equate with popularity? The answer depends on how attitudes to genetically modified crops change as they become ever more widely grown in countries such as the USA, China, Argentina, and Brazil, and maybe even in Western Europe. If no adverse effects of the genetically modified materials are reported it may alter the public's attitude to, and demand for, genetically modified rice—a product that could substantially raise yields per hectare without requiring more nitrogen and water.

Regardless of how the second green revolution is engineered, nature's remarkable C_4 revolution continues and its momentum is likely to carry it forward for decades to come. The rapidly rising global carbon dioxide content of the atmosphere is not expected to halt or reverse its progress; the C_4 genie is out of the evolutionary lamp. True, carbon dioxide fertilization is expected to stimulate tree growth and favour the spread of woody plants into grasslands. But a far more significant issue is the magnitude and pace of human intensification of land use.[86] Since the seventeenth century, 12 million square kilometres of forest have been cleared for crop production, and tropical deforestation continues apace. In Amazonia, the conversion of forest to pasture is already increasing the accidental ignition and severity of fires to the point where fire now threatens the integrity of large areas of tropical forest by accelerating its conversion to C_4 savanna.[87] Thanks to humankind's intervention, the pace of nature's green revolution looks set to quicken.